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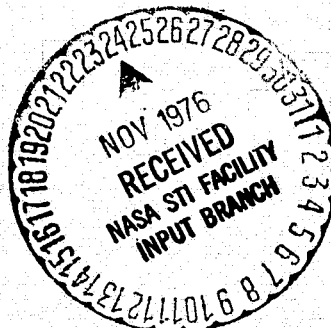
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OPTIMIZED SELECTIVE COATINGS FOR SOLAR COLLECTORS

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ABSTRACT

The spectral reflectance properties of black nickel electroplated over stainless steel and of black copper produced by oxidation of copper sheet have been measured for various plating times of black nickel and for various lengths of time of oxidation of the copper sheet, and compared to black chrome over nickel and to converted zinc. It was determined that there was an "optimum" time for both plating of black nickel and for the oxidation of copper to copper black. At this time the solar selective properties show high absorptance in the solar spectrum and low emittance in the infrared. The conditions are compared for production of optimum optical properties for black nickel, black copper, black chrome, and two black zinc conversions which at the same conditions had absorptances of 0.84, 0.90, 0.95, 0.84, and 0.92, respectively, and emittances of 0.18, 0.08, 0.09, 0.10, and 0.08, respectively.

INTRODUCTION

The NASA Lewis Research Center is conducting research on flat plate solar collectors as part of the national program to develop new energy sources. In order to achieve high collector-plate temperatures, it is important that the collector have a "selective" coating, that is, one that has both maximum absorptance across the solar spectrum and the minimum possible emittance in the infrared (ref. 1).

In the present report a procedure is presented for determining the time of formation which produces an "optimum" absorptance and emittance combination for black copper, black nickel, black chrome, and black zinc. The preparation of each of these coatings can be adjusted to give this optimum combination of absorptance greater than 0.90 and emittance less than 0.10.

DESCRIPTION OF SPECTRAL MEASUREMENTS

The absorptance and emittance of each surface was calculated from measurements of the hemispherical diffuse reflectance. The spectral reflectance of the black coating was measured at wavelengths from 0.35 to 2.1 micrometers with a

Cary-14 spectrophotometer with a spherical diffuse reflectance attachment. A calcium carbonate (CaCO_3) surface prepared at the NASA Lewis Research Center was used as a standard.

The spectral reflectance was measured at wavelengths from 0.3 to 18.0 micrometers with a Willey 318-A spectrophotometer using a spherical diffuse reflectance attachment. The Willey 318-A is a Michelson interferometer type of spectrophotometer. Evaporated gold film was used as a standard. Evaporated aluminum on glass was used as a secondary standard. The accuracy of measurement is estimated to be ± 0.02 units of reflectance.

PREPARATION OF COATINGS

In this investigation all of the black coatings were produced on 4- by 6-inch test panels. For the black nickel these test panels were polished 304 stainless steel; for the black copper, they were polished sheet copper; and for the black chrome and black zinc, they were 1020 cold rolled steel polished on one surface to a roughness of less than $1/2$ microinch rms.

Black Nickel

The black nickel was formed on the stainless steel panels by plating for various periods of time from a sulfate bath containing:

Nickel sulfate, oz/gal (g/liter)	14 (105)
Ammonium sulfate, oz/gal (g/liter)	2 (15)
Zinc sulfate, oz/gal (g/liter)	5 (37)
Sodium thiocyanate, oz/gal (g/liter)	2 (15)

At a constant:

pH	5.6 to 5.9
Temperature, $^{\circ}\text{F}$ ($^{\circ}\text{C}$)	75 (24)
Current density, A/ft^2 (mA/cm^2)	0.8 (0.8)

After removal from the plating, both the panels were water rinsed, alcohol rinsed and air dried.

Black Copper

The oxidation of the copper test panels was made with Enthone Co., Ebonol-C for various times at the concentration and temperature conditions specified by Enthone. For increasing times of oxidation the general appearance of the panels varied from the untreated copper to a very intense, jet black.

Black Chrome and Black Zinc

The black chrome and black zinc surfaces were prepared as described in references 2 and 3, respectively.

TEST RESULTS

The black nickel was plated at various times up to 30 minutes and the resultant reflectances are shown in figure 1. For clarity, only the results for times of 0, 2, 6, and 15 minutes are shown in figure 1. While the visible reflectances of black nickel rapidly decreases with plating time, the increasing plating time produces a structure which gives systematic, reoccurring maxima and minima in the reflectance curve. These increase in both amplitude and in cycle length as plating time is increased.

The results of the spectral measurements of the reflectance of the black copper panels oxidized for various times up to 4 minutes are shown in figure 2. For clarity, only the reflectance curves for 0, 1/4, 1/2, and 4 minutes oxidation are shown. In general there is a very rapid decrease in visible reflectance. At the longer times of oxidation there is a considerable decrease in infrared reflectance. The reflectance of an idealized solar selective coating is also included.

The reflectance of black chrome electroplated at various times is shown in figure 3. The reflectance of the black zinc produced by two conversion processes (chromate and chloride) are shown in figures 4 and 5.

The absorptances and emittances as calculated from the measured reflectances for various formation times are summarized in table I for each of the five black coatings.

DISCUSSION OF RESULTS

The values of the absorptance integrated over the solar spectrum versus the integrated emittance corresponding to a coating temperature of 250° F is shown in figures 6 to 10 for each of the black coatings. The values of absorptance and emittance were calculated from the measured values of the total diffuse reflectance versus wavelength as shown in figures 1 to 5. Figures 6 to 10 show the generally identical behavior of each of these materials in that as the time of formation of coating is increased, there is an initial rapid increase in absorptance with only a minimal accompanying increase in emittance. Then, after approaching "saturated" values of absorptance, the emittance increases more rapidly. Therefore, a time of coating formation may be selected for any of the black coatings - copper, chrome, zinc, or nickel - which gives the maximum absorptance

with the minimum emittance. The figures show that each of these black coatings can be suitably "optimized" by simple control of the time of coating formation to produce the desired optical selectivity of high absorptance and low emittance.

The exact value of absorptance and emittance which are the most optimum are obtained by maximizing the difference between energy absorbed in the visible (short) wavelengths and the energy reradiated in the infrared (long) wavelengths. Since the emittance increases with temperature and the total energy reradiated is strongly dependent on temperature, the best combination of values of absorptance and emittance is dependent on the temperature selected for operating the coating. To compare the various coatings, values of absorptance and emittance were determined for each coating at preparation times at which the change in absorptance to the change in emittance ($\Delta\alpha/\Delta\epsilon$) had an arbitrarily selected value of 1.0, as discussed in reference 2. These values of absorptance and emittance are shown in figure 11 for the five black coatings. At values of $\Delta\alpha/\Delta\epsilon < 1.0$, additional preparation time increases emittance, and thus heat lost by radiation, faster than it increases absorption or heat capture.

Based strictly on optical properties the ideal solar selective coating would have a visible absorptance approaching 1.0 and an infrared emittance approaching 0.0 as shown by the arrows in figure 11. This illustrates a method of rating coatings based entirely on optical properties. The relatively low merits, based on optical properties, of the black nickel used in this study is largely caused by the inherently high emittance of the stainless steel used as a substrate. If the black nickel were plated on copper or on nickel such as used for the black chrome, both of which have an intrinsic emittance lower than stainless steel, then the black nickel would have a higher merit.

In addition to optical properties, practical manufacturing considerations such as cost, availability, durability, and the number of steps required for coating application are also important factors in the selection of a particular solar coating.

SUMMARY OF RESULTS

Measurements of the spectral reflectance of black nickel, black copper, black chrome and both chromate and chloride converted black zinc have been made at wavelengths from 0.35 to 18 microns and calculated values of integrated solar spectrum absorptance and infrared emittance are presented. The variation of emittance with absorptance is shown for each of the five black coatings. The relative merit of each coating was determined from its emittance versus absorptance relationship by arbitrarily selecting the combination of these properties where the change of emittance is equal to the change of absorptance. On this

basis and for the combination of coatings and substrates studied, black chrome on nickel is the most effective coating followed by black zinc (chloride conversion) on zinc, and black copper on copper.

REFERENCES

1. Tabor, H., Selective Radiation I - Wavelength Discrimination, Transactions of the Conference on the Use of Solar Energy, Vol. 2, Pt. 1, Sec. A. F. Carpenter, ed., University of Arizona Press, 1958, pp. 24-33.
2. McDonald, G. E., and H. B. Curtis, Variation of Solar-Selective Properties of Black Chrome with Plating Time, NASA Technical Memo. X-71731, May 1975.
3. McDonald, G. E., H. B. Curtis, and L. Gianelos, Spectral Reflectance Properties of Electroplated and Converted Zinc for Use as a Solar Selective Coating, NASA Technical Memo. X-71817, Dec. 1975.

TABLE I. - SOLAR SPECTRUM ABSORPTANCE AND 250° F BLACKBODY EMITTANCE
AT VARIOUS COATING FORMATION TIMES

	Absorptance emittance	Coating formation time, min										
		1/4	1/2	3/4	1	2	4	6	8	10	15	30
Black nickel	α					0.80	0.85	0.85	0.88	0.89	0.89	0.89
	ϵ					0.16	0.20	0.28	0.35	0.44	0.69	0.82
Black copper	α	0.79	0.90		0.91	0.93	0.94					
	ϵ	0.04	0.08		0.05	0.19	0.44					
Black chrome	α	0.64	0.87		0.96	0.96	0.95			0.94		
	ϵ	0.04	0.06		0.10	0.12	0.17			0.34		
Black zinc (chromate)	α	0.79	0.87	0.92	0.93	0.92						
	ϵ	0.05	0.10	0.37	0.73	0.53						
Black zinc (chloride)	α	0.93	0.95	----	0.96	0.97						
	ϵ	0.08	0.12	----	0.21	0.73						

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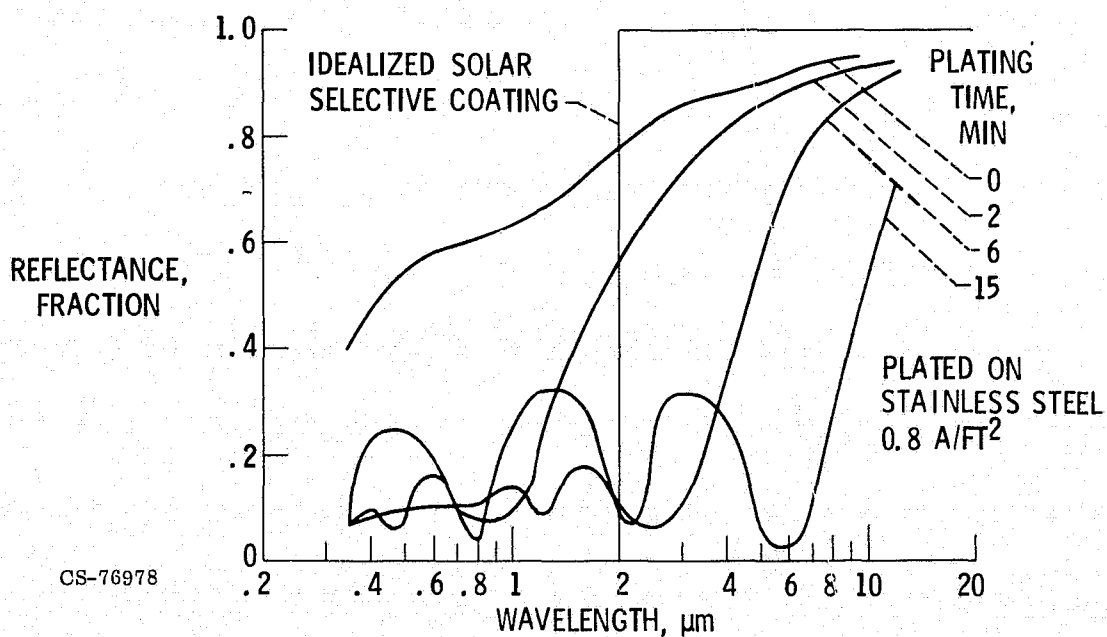


Figure 1. - Reflectance of black nickel versus wavelength.

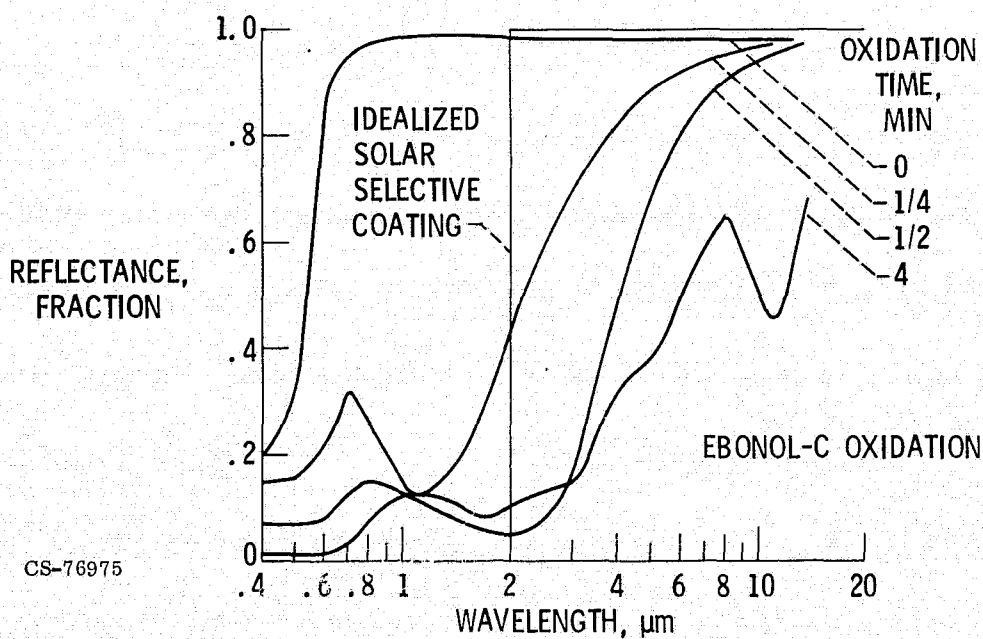


Figure 2. - Reflectance of black copper versus wavelength.

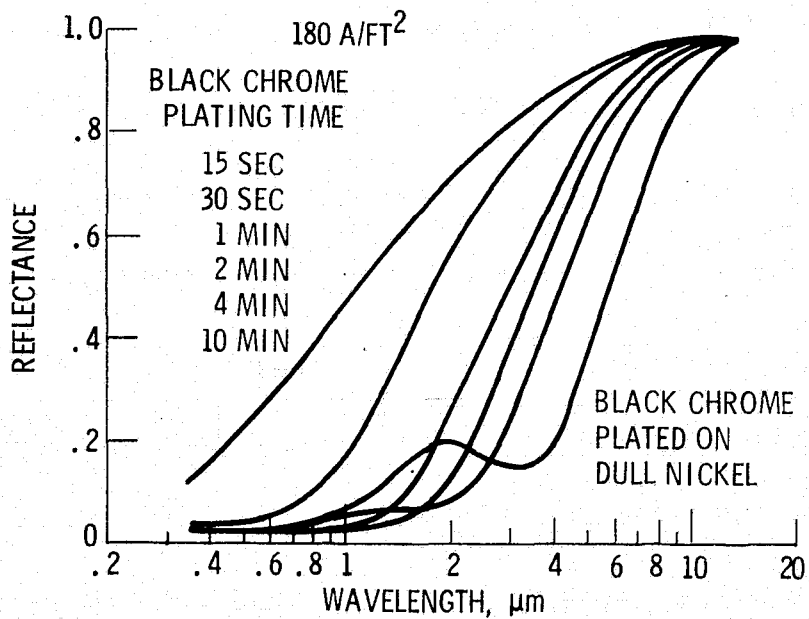


Figure 3. - Reflectance of black chrome versus plating time.

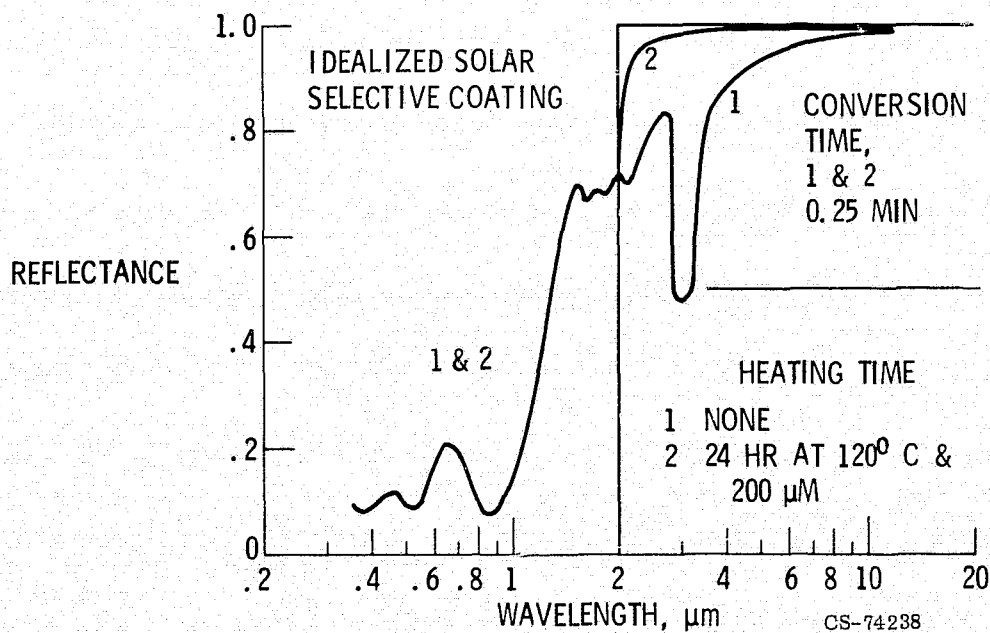


Figure 4. - Reflectance of black zinc produced by 1/2 concentration chromate conversion.

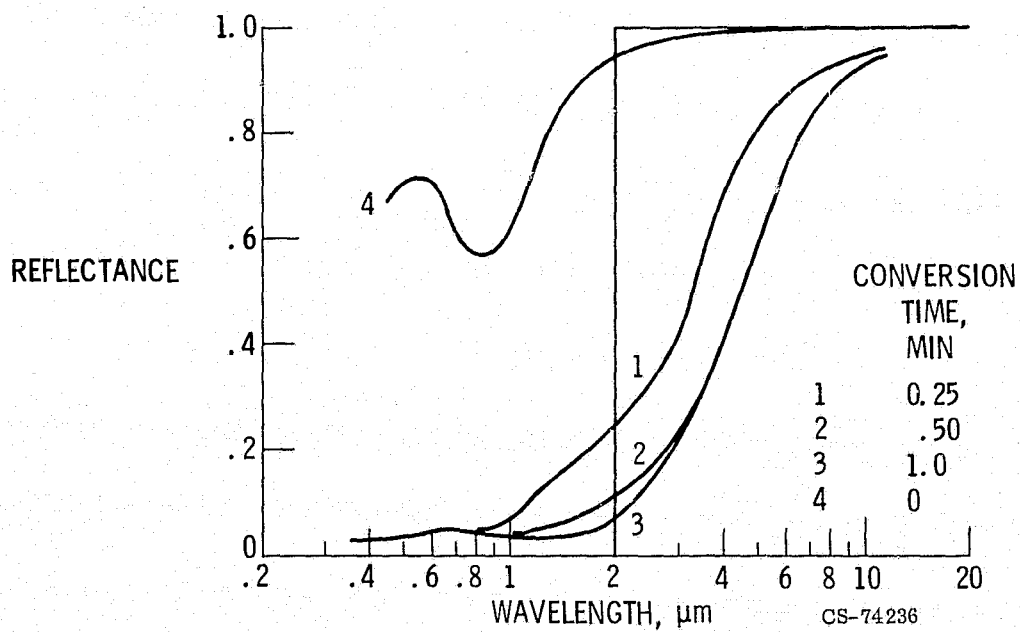


Figure 5. - Reflectance of black zinc produced by chloride conversion.

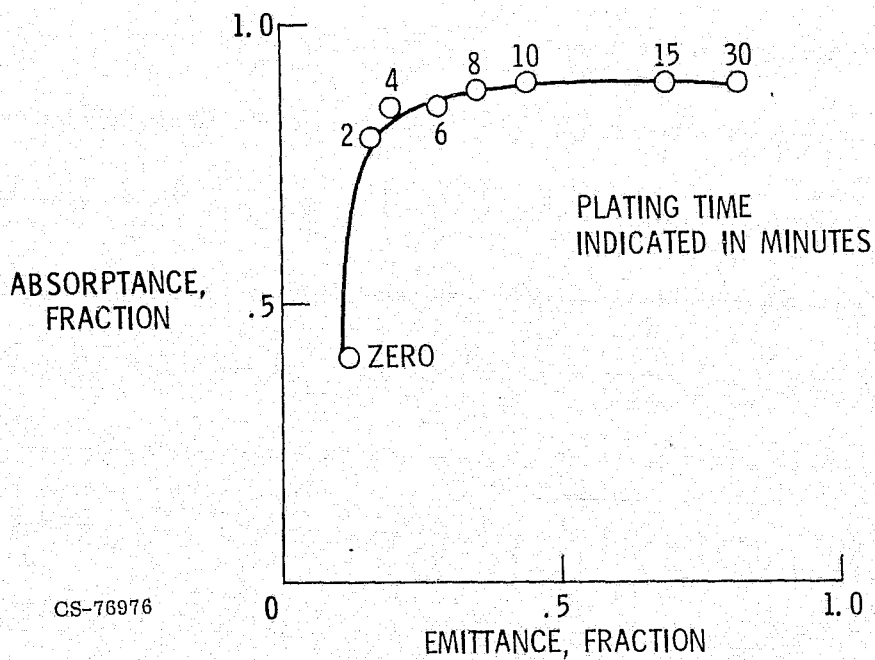


Figure 6. - Solar absorptance versus infra-red emittance for black nickel plated on stainless steel.

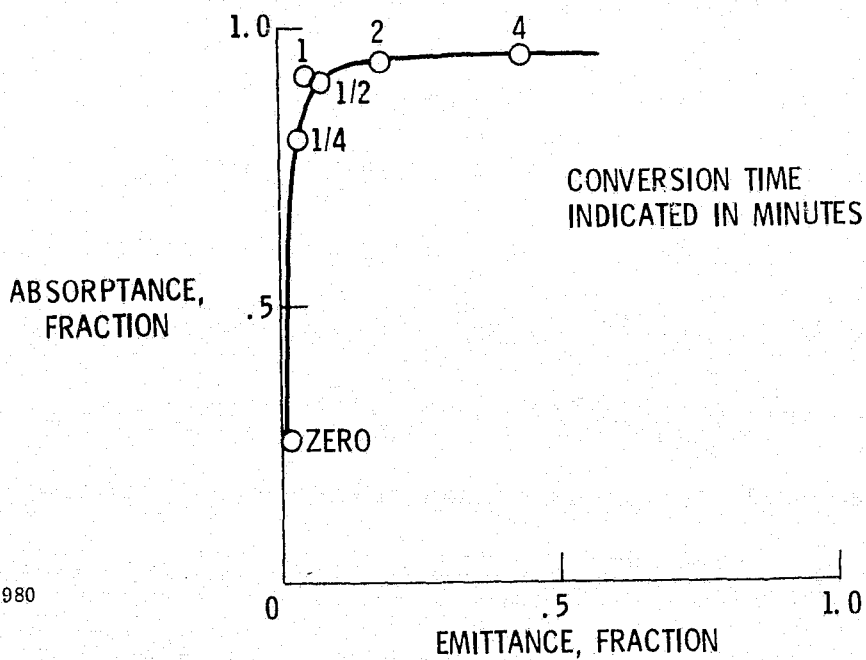


Figure 7. - Solar absorptance versus infra-red emittance for black copper.

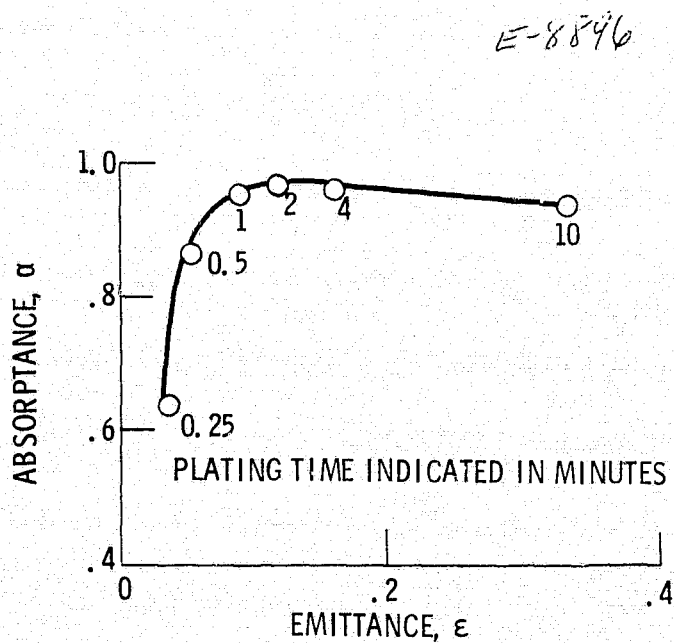


Figure 8. - Solar spectrum absorptance versus infra-red emittance for black chrome on dull nickel.

CONVERSION TIME INDICATED IN MINUTES FOR CHROMATE CONVERSION
AT 1/2 CONCENTRATION ONLY

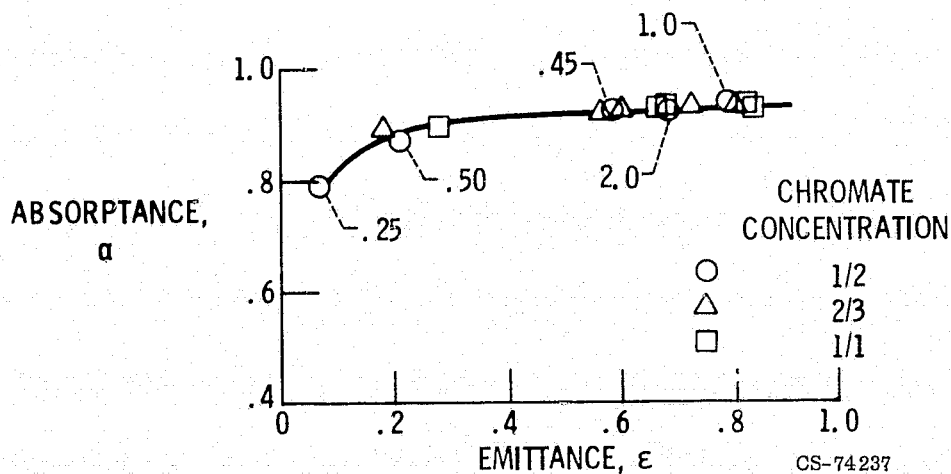


Figure 9. - Solar spectrum absorptance versus infra-red emittance for black zinc on zinc produced by chromate conversion.

CONVERSION TIME INDICATED IN MINUTES

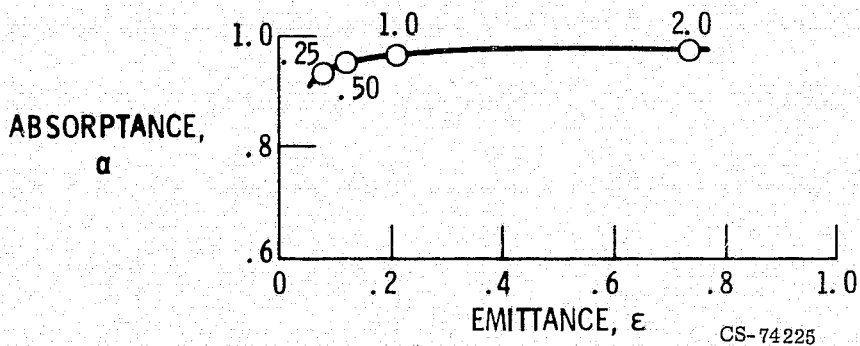


Figure 10. - Solar spectrum absorptance versus infra-red emittance for black zinc produced by chloride conversion.

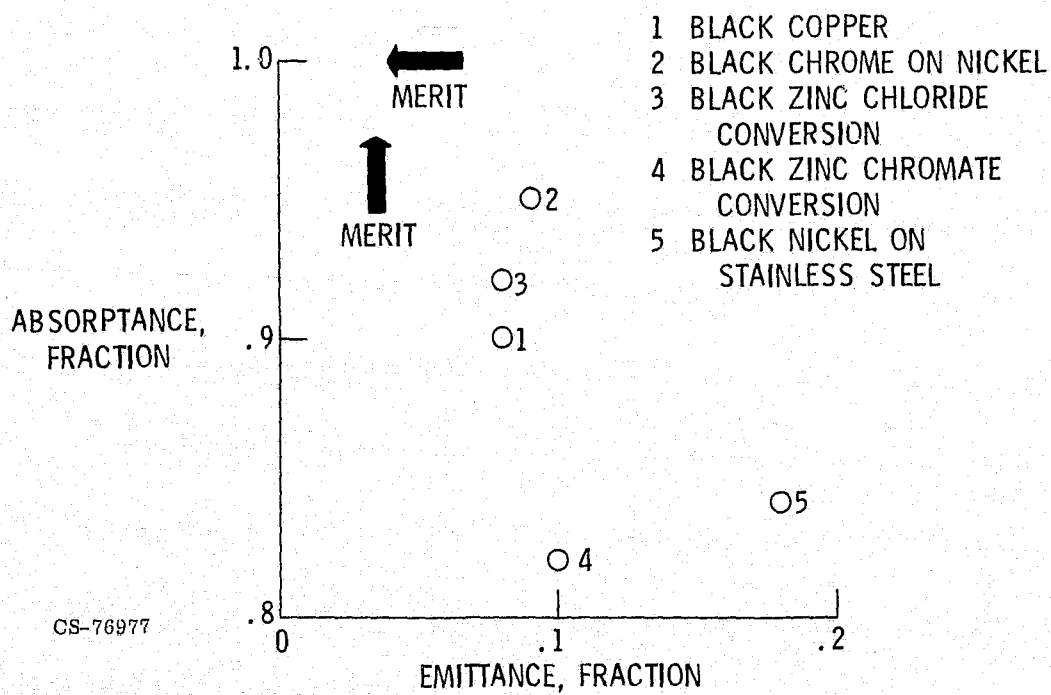


Figure 11. - Absorptance versus emittance of various coatings.